

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Shoji HARA et al.

Appn. No.: 09/782,169

Group Art Unit: 1782

Filed: February 14, 2001

Examiner: Brian K. Talbot

For: Laminate Comprising Polyimide and Conductor Layer, Multi-Layer Wiring Board with the Use of the Same and Process for Producing the Same

DECLARATION UNDER 37 C.F.R. §1.132

Assistant Commissioner of Patents  
Washington, D.C. 20231

Sir/Madam:

I, Masaru NISHINAKA, do declare and state that:

I graduated from Osaka City University, Faculty of Engineering, Department of Applied Physics, with a degree in Industry, receiving a Master's Degree in March of 1992.

Since April of 1992, I have been employed by KANEKA CORPORATION, where I am engaged in research and development relating to the synthesis of polyimide filmsarticles, the surface treatments, and the metallizing.

I am familiar with the prosecution history of the above-identified application including the Office Action dated February 24, 2003 in the above-identified application.

I am a co-inventor of the invention described and claimed in the above-identified application.

The following experiment was conducted by me or my direct supervision in order to demonstrate the superiority of the present invention.

EXPERIMENTATION

1. Referential Example 3

In the Example 2 in the present specification, a laminate which does not include the thermoplastic polyimide was prepared, and the peel strength thereof was measured.

A 17% by weight solution of a polyamic acid, which had been synthesized by using pyromellitic dianhydride/p-phenylene(trimellitic acid monoester acid anhydride)/p-phenylenediamine/4,4'-diaminodiphenyl ether at a molar ratio of 5/5/4/6, in DMF was defoamed by centrifugation and then cast on an aluminum foil to give a final thickness of 17  $\mu\text{m}$ . This laminate comprising the aluminum foil and the polyamic acid solution was heated to 110°C for 4 minutes to thereby give a self-supporting gel film. This gel film was heated to 150°C, 200°C, 250°C, 300°C and 350°C each for 1 minute to thereby give non-thermoplastic polyimide films of 17  $\mu\text{m}$  in thickness.

These non-thermoplastic films thus obtained were each set on a substrate holder of a magnetron sputtering apparatus HSM-720 (manufactured by Shimadzu Corporation) and the apparatus was evacuated to  $4 \times 10^4 \text{ Pa}$ . Subsequently, Ar gas was blown so that the pressure within the magnetron sputtering apparatus was maintained at 0.6 Pa. In this state, a thin copper film of 0.1  $\mu\text{m}$  in thickness was formed on the film by using a copper target with a DC power source of a current value of 0.5A. Before the formation of the thin film, pre-sputtering was carried out for 15 minutes. Thus, 3 samples each having a copper thin film formed on a non-thermoplastic film were prepared. Then these samples were cut into pieces of 12 cm x 8 cm and subjected to electrolytic copper

plating by the electrolytic plating method while passing an electric current (2 A) until the conductor thickness attained 20  $\mu\text{m}$ . Each sample was allowed to stand at room temperature for 4 days and then heated at 220°C for 30 minutes.

Subsequently, the copper oxide film formed on the conductor layer surface was eliminated by using a 5% by weight sulfuric acid solution. After applying a circuit tape of 3 mm in width, etching was performed with the use of a cupric chloride solution. After taking off the circuit tape, the sample was dried at 50°C for 30 minutes to give a pattern of 3 mm in width. Next, the peel strength of the pattern of 3 mm in width was determined. The peel strength was measured by pulling in a direction 90° to the polyimide at a speed of 50 mm/min. The peel strength was measured thrice and the average was employed. Table 1 summarizes the measurement results.

## 2. Referential Example 4

In the Example 4 in the present specification, a laminate which does not include the thermoplastic-polyimide was prepared, and the peel strength thereof was measured.

A 17% by weight solution of a polyamic acid, which had been synthesized by using pyromellitic dianhydride/p-phenylene(trimellitic acid monoester acid anhydride)/p-phenylenediamine/4,4'-diaminodiphenyl ether at a molar ratio of 5/5/4/6, in DMF was defoamed by centrifugation and then cast on an aluminum foil to give a final thickness of 17  $\mu\text{m}$ . This laminate comprising the aluminum foil and the polyamic acid solution was heated to 110°C for 4 minutes to thereby give a self-supporting gel film. This gel film

was heated to 150°C, 200°C, 250°C, 300°C and 350°C each for 1 minute to thereby give non-thermoplastic polyimide films of 17  $\mu\text{m}$  in thickness.

These non-thermoplastic films thus obtained were each set on a substrate holder of a magnetron sputtering apparatus HSM-720 (manufactured by Shimadzu Corporation) and the apparatus was evacuated to  $4 \times 10^{-4}$  Pa. Subsequently, Ar gas was blown so that the pressure within the magnetron sputtering apparatus was maintained at 0.6 Pa. In this state, a thin copper film of 0.3  $\mu\text{m}$  in thickness was formed on the film by using a copper target with a DC power source of a current value of 0.5A. Before the formation of the thin film, pre-sputtering was carried out for 15 minutes. Thus, 6 samples each having a copper thin film formed on a non-thermoplastic film were prepared. Then these samples were cut into pieces of 12 cm x 8 cm and coated on both faces by using a fluoroplastic film sheet (Niftron manufactured by Nitto Denko Corporation) of 0.2 mm in thickness. Further, both faces of these samples were coated with a rubber sheet of 5 mm in thickness and a ferro-plate. Then these samples were pressed under a pressure of 3 MPa for 10 minutes at the pressing temperature of 220°C.

After surface-washing with a 5% aqueous solution of sulfuric acid for 30 seconds, these samples were subjected to electrolytic copper plating by the electrolytic plating method while passing an electric current (2 A) until the conductor thickness attained 15  $\mu\text{m}$ . Each sample was allowed to stand at room temperature for 4 days. After applying a circuit tape of 3 mm in width, etching was performed with the use of a cupric chloride solution. After taking off the circuit tape, the sample was dried at 50°C for 30 minutes to give a pattern of 3 mm in width. Next, the peel strength of the pattern of 3 mm in width

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was determined. The peel strength was measured by pulling in a direction 90° to the polyimide at a speed of 50 mm/min. Table 2 summarizes the measurement results.

[Table 1]

	Process	Heating temp. (°C)	Peel strength (N/cm)
Ex. 2 (a sputtering layer / a thermoplastic polyimide / a non- thermoplastic polyimide )	Sputtering → Electroplating → Heating	170	4.2
		220	4.4
Comp. Ex. 2 (a sputtering layer / a thermoplastic polyimide / a non- thermoplastic polyimide )	Sputtering → Electroplating	no	1.8
Referential Ex. 1 (a sputtering layer / a non- thermoplastic polyimide )	Sputtering → Electroplating	no	1.0
Referential Ex. 3 (a sputtering layer / a non- thermoplastic polyimide )	Sputtering → Electroplating → Heating	220	1.1

[Table 2]

	Process	Heating temp. (°C)	Peel strength (N/cm)
Ex. 4 (a sputtering layer / a thermoplastic polyimide / a non-thermoplastic polyimide )	Sputtering → Heating and Pressurizing → Electroplating	170	4.2
		220	5.0
		250	5.6
Comp. Ex. 4 (a sputtering layer / a thermoplastic polyimide / a non-thermoplastic polyimide )	Sputtering → Electroplating	no	1.8
Referential Ex. 2 (a sputtering layer / a non- thermoplastic polyimide )	Sputtering → Electroplating	no	0.9
Referential Ex. 4 (a sputtering layer / a non- thermoplastic polyimide )	Sputtering → Heating and Pressurizing → Electroplating	220	0.8

### Conclusion

From the results as above, in a laminate wherein a conductor layer was formed directly on a non-thermoplastic polyimide, the improvement of the adhesive strength could not be considered even though heating or heating and pressurizing were conducted.

However, in the present invention, the adhesive strength of the laminate was extremely improved due to the existence of a thermoplastic polyimide and heating treatment.

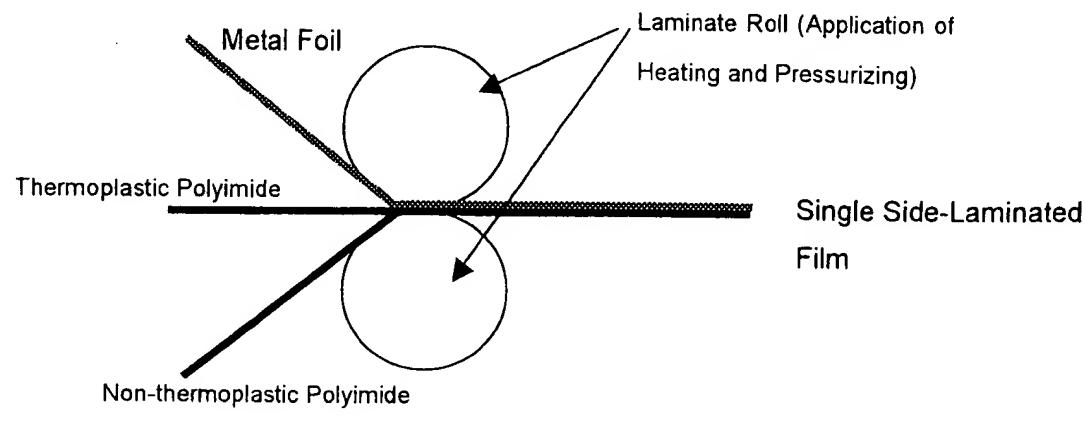
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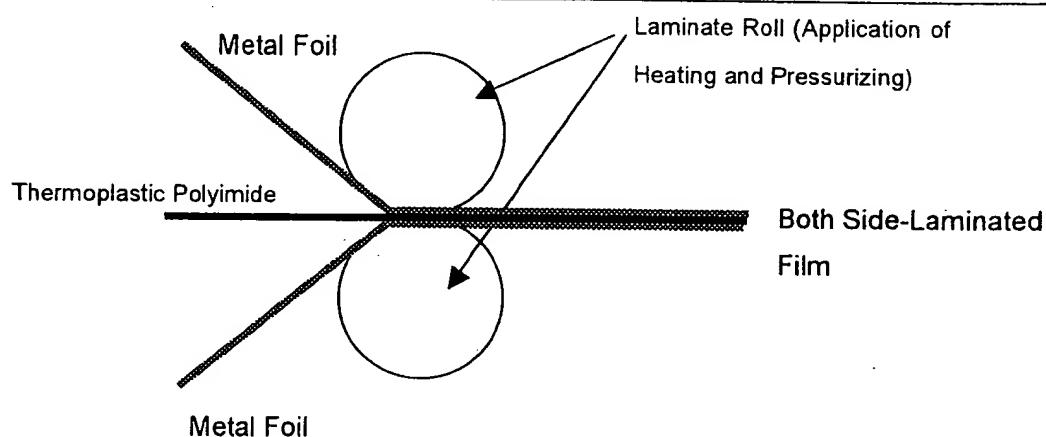
I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, at Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: June 23rd, 2023 Name: Masaru Nishinaka

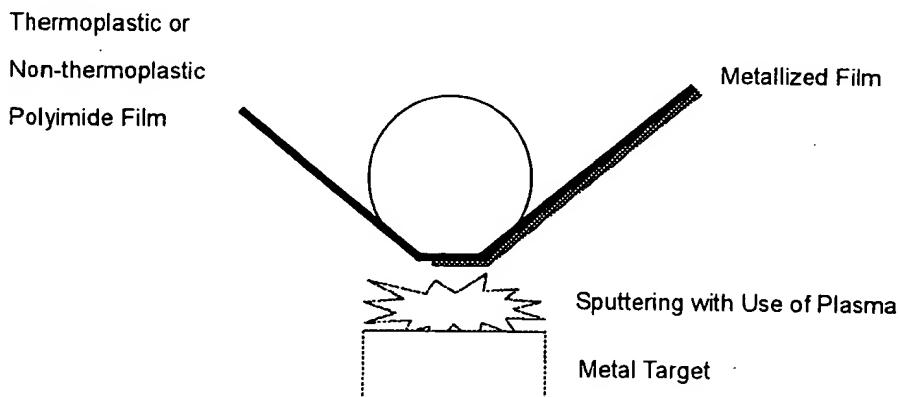
Masaru NISHINAKA



Schematic Illustration of Heat Lamination Method (1)



Schematic Illustration of Heat Lamination Method (2)



Schematic Illustration of Sputtering Method